



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number:

0 468 465 A1

③

EUROPEAN PATENT APPLICATION

① Application number: 91112356.0

② Int. Cl.³ G03G 9/09, C09D 11/00

③ Date of filing: 23.07.91

④ Priority: 23.07.90 JP 194187/90

⑤ Date of publication of application:
29.01.92 Bulletin 92/05⑥ Designated Contracting States:
CH DE FR GB LI NL⑦ Applicant: SHOWA DENKO KABUSHIKI
KAISHA13-9, Shiba Daimon 1-chome
Minato-ku, Tokyo 105(JP)⑧ Inventor: Murofushi, Katsumi, c/o Showa
Denko K.K.Kagakuhin, Kenkyusho, 5-1, Ogimachi
Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)Inventor: Hosoda, Yoshikazu, c/o Showa
Denko K.K.

Kagakuhin, Kenkyusho, 5-1, Ogimachi,

Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)

Inventor: Gan, Yoko, AI, c/o Showa Denko K.K.

Kagakuhin, Kenkyusho, 5-1, Ogimachi

Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)

Inventor: Kondo, Kunio, c/o Showa Denko K.K.

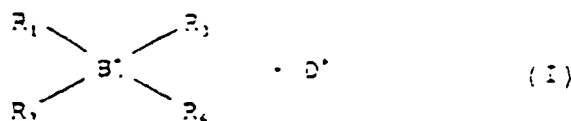
Kagakuhin, Kenkyusho, 5-1, Ogimachi

Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)

⑨ Representative: Strehl, Schüdel-Hopl,
GroeningMaximilianstrasse 54 Postfach 22 14 55
W-8000 München 22(DE)

⑩ Near infrared ray-decolorizable recording material.

⑪ The present invention relates to a near infrared ray-decolorizable recording material comprising a near infrared ray-absorbing cationic dye-borate anion complex having the formula (I):



wherein D^+ represents a cationic dye having absorptions in the near infrared region; R_1 , R_2 , R_3 , and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkynyl, silyl, alkoxy, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_1 , R_2 , R_3 , and R_4 represents an alkyl group having 1 to 8 carbon atoms.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a near infrared ray-decolorizable recording material capable of being decolorized with a near infrared ray, and a toner and ink containing the near infrared ray-decolorizable recording material as a colorant.

(2) Description of the Related Art

Conventionally, in the fields of, for example, printing and copying, the storability of a recording material, in terms of environmental resistance, e.g., light resistance, moisture resistance, resistance to solvent, and thermal resistance, has become increasingly important, and thus many attempts have been made to improve the physical properties of dyes and pigments. Particularly, many developments have been made in the fields of electrophotographic recording, electrostatic recording, and thermal transfer-ink recording. Recently, due to the increasing amount of information available, a repeated printing has been required, and photochromic materials and thermochromic materials have been developed as recording materials for multiple recording systems or rewritable recording materials (see, for example, Japanese Unexamined Patent Publication (Kokai) No. 60-155179, Japanese Unexamined Patent Publication (Kokai) No. 50-75991, and Japanese Unexamined Patent Publication (Kokai) No. 50-105555).

Japanese Unexamined Patent Publication (Kokai) No. 60-155179 discloses fluide compounds which appear blue under ultraviolet rays and are transparent under a white light, and Japanese Unexamined Patent Publication (Kokai) No. 50-75991 discloses a thermally discoloring material comprising a coupler consisting mainly of a leuco-dye, and a phenolic hydroxy group-containing compound as a developer. These rewritable recording materials, however, are reversibly decolorized and colored or subjected to color changes by a visible light or ultraviolet rays, and further, have problems in terms of storage stability under visible light and durability to repeated recording.

Further, many similar studies have been made in the fields of electrophotographic recording and electrostatic recording, as well as in the fields of printing inks and inks for printers, and many electrophotographic printing methods are known, for example, as disclosed in U.S. Patent No. 2297691, Japanese Examined Patent Publication (Kokoku) No. 42-20910, and Japanese Examined Patent Publication (Kokoku) No. 43-24748. In general, an electric latent image is formed on a sensitized material, utilizing a photoconductive substance in many ways, the latent image is developed with a toner to form a visible image, and optionally, after the toner image is transferred to a material such as paper, the image is fixed by the application of heat and pressure to obtain a copy. Furthermore, various developing processes wherein an electrostatic image is obtained by using a toner are known. For example, various developing processes, such as the magnetic brush process disclosed in U.S. Patent No. 2674063, the cascade developing process disclosed in U.S. Patent No. 2618552, the powder-cloud process disclosed in U.S. Patent No. 2221776, the fur brush developing process, and the liquid developing process, etc. are known. Various magnetically recording processes wherein a magnetic latent image is formed and then developed with a magnetic toner are also known. The toner image when developed is optionally transferred to a material such as paper, and then fixed. As processes for developing the toner image, a process wherein the toner is heated and melted by a heater or heated roller, to be fused to a base material and followed by solidification, a process wherein the binder resin of the toner is softened or dissolved with an organic solvent to be fixed on a base material, and a process wherein the toner is fixed on a base material by the application of pressure are known.

The toners used in the fixing process using heating rollers as described above are generally prepared by melt mixing and uniformly dispersing a colorant such as carbon black, and additives such as an electric charge regulator, in a thermoplastic resin such as a styrene-butyl acrylate copolymer, allowing the mixture to cool, and then finely pulverizing the solidified product into a desired particle diameter by a pulverizer or dispersing machine. Furthermore, currently a coloration is under development in the printing and copying fields, and an improvement of the physical properties of colorants and electric charge regulator is widely sought (see, for example, Japanese Unexamined patent publication (Kokai) No. 57-130046 and Japanese Unexamined patent publication (Kokai) No. 57-131650).

Many printing processes, such as offset press printing, letterpress printing, gravure printing, transfer press printing, or specific press printing inclusive of flexographic printing, metal printing, plastic printing, and glass printing, as well as electric printing by printers such as impact printers or non-impact printers in the printing field are known, and the inks used consist mainly of a vehicle, a binder, and a colorant such as a dye or pigment. Further, recently, the development of ultraviolet curing inks for preventing pollution by not

using solvents, improving productivity by a rapid curing, or improving the physical properties of the cured coat have been proposed (see, for example, Japanese Unexamined patent publication No. 1-229084, Japanese Unexamined patent publication (Kokai) No. 1-271469, and Japanese Unexamined patent publication (Kokai) No. 2-22370).

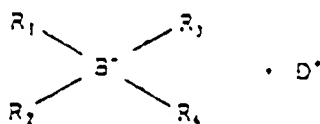
- 5 Nevertheless, thermal color-changing materials such as the photochromic material and leuco-dye as described above have a poor image stability under visible light. Furthermore, the above-mentioned toners for electrophotographic recording and printing inks have problems in that, after being set, the set image cannot be decolorized, the recording portion cannot be set again, and the recording paper can not be reused, and further, in an accompanying disposal treatment a problem arises in keeping the content of disposed papers secret.

SUMMARY OF THE INVENTION

- An object of the present invention is to provide a recording material having sensitivity to light in the near infrared region, to stabilize the recorded portion, capable of decolorizing the set and printed recording material with near infrared rays and of recording on the same portion again, and stable under visible light.

- To solve the above problems, investigations were made on a specific near infrared ray-absorbing cationic dye-borate anion complex, and as a result, it was found that a near infrared ray decolorizable recording material, which is decolorized with near infrared rays, can be obtained, and thus the present invention was achieved.

- In accordance with the present invention, there is provided a near infrared ray-decolorizable recording material comprising a near infrared ray-absorbing cationic dye-borate anion complex having the formula (I):



- wherein D^+ represents a cationic dye having absorptions in the near infrared region; R_1 , R_2 , R_3 , and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_1 , R_2 , R_3 , and R_4 represents an alkyl group having 1 to 8 carbon atoms,

having absorptions in the near infrared region, which is decomposed and decolorized by an irradiation of near infrared rays having a wavelength of 700 nm or more, and which is stable under visible light.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The near infrared ray-decolorizable recording material according to the present invention can provide a light decolorizable composition sensitive to near infrared rays, which can be decolorized by irradiating light having this wavelength region, by incorporating it into a base material such as a wax or resin.

- The specific types of cationic dyes which compose the near infrared ray-absorbing cationic dye-borate anion complex used in the present invention are cyanine, triarylmethane, aminium, and dimonium dyestuffs which have absorptions in the near infrared region. R_1 , R_2 , R_3 , and R_4 in the borate anion independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_1 , R_2 , R_3 , and R_4 represent an alkyl group having 1 to 8 carbon atoms. Examples of the substituents for the above-mentioned substituted groups are methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-octyl, cyclohexyl, cyclohexenyl, methoxy methyl, methoxyethyl, dimethylaminoethyl, phenyl, arsyl, ethoxy phenyl, methyl phenyl, t-butyl phenyl, fluorenyl, chlorophenyl, dimethylaminophenyl, diethylaminophenyl, vinyl, allyl, triphenylsilyl, dimethylphenylsilyl, dibutylphenylsilyl, trimethylsilyl, piperidyl, thienyl, furyl, pyrrolyl, etc.

Examples of the complexes especially available in the present invention are shown in Table 1.

EP 0 468 465 A1

Table 1

Complex No.	Structure	R	Ar	λ_{max} (THPT)
1				820nm
2				830nm
3-A			n-butyl phenyl	822nm
3-B			n-hexyl anisyl	822nm
3-C			n-octyl phenyl	822nm
4				768nm
5-A			n-butyl phenyl	748nm
5-B			n-hexyl anisyl	748nm
5-C			n-octyl phenyl	748nm

Table 1 (continued)

Complex No.	Structure	R	Ar	λ_{max} (TMPT)
4-A		n-butyl phenyl		785nm
4-B		n-hexyl anisyl		785nm
4-C		n-octyl phenyl		785nm
7-A		n-butyl phenyl		828nm
7-B		n-hexyl anisyl		828nm
7-C		n-octyl phenyl		828nm
9				787nm
9				819nm
10				1060nm

Note

λ_{max} absorption wavelength
TMPT: trimethylolpropane trimethacrylate

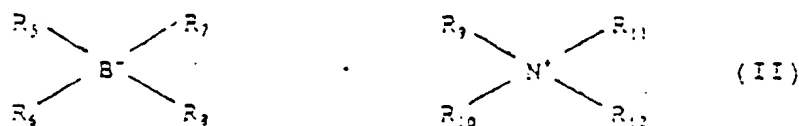
Phenyl group

The waxes among the base materials usable in the present invention are those generally used in thermal transferring sheets and inks, including, for example, carnauba wax and Japan wax, which are vegetable waxes; beeswax and wool grease, which are animal waxes; paraffin wax and microcrystalline wax, which are mineral waxes; and polyethylene waxes, PTFE, chlorinated paraffin, and fatty acid amides, which are synthetic waxes.

The resins usable in the present invention are all conventional resins, and include, for example, normal temperature drying and curing resins for coating, moisture curing resins for coating, and thermal curing resins for coating, etc., which are capable of brushing, spray coating, dip coating, gravure coating, doctor coating, roll coating, electrostatic coating, powder coating, transferring, and priming, etc. Concrete examples include oil varnish, boiled oil, shellac, cellulose resins, phenol resins, alkyd resins, amino resins, xylene resins, toluene resins, vinyl chloride resins, vinylidene chloride resins, vinyl acetate resins, polystyrene resins, vinylbutyral resins, acrylic resins, methacrylic resins, diallyl phthalate resins, epoxy resins, urethane resins, polyester resins, polyether resins, amine resins, furan resins, polyimide resins, silicone resins, and fluoroplastics. Furthermore, the resins may be photo- and electron beam-curing resins, concrete examples including macromonomers, oligomers, and monomers of polyvinyl cinnamate resins, polyvinylbenzalacetophenone resins, polyvinylstyryl pyridine resins, polyvinyl anthral resins, unsaturated polyester resins, acrylated oils, acrylated alkyd resins, acrylated polyester resins, acrylated polyether resins, acrylated epoxy resins, acrylated polyurethane resins, acrylic resins, acrylated sperane resins, acrylated silicone resins, acrylated fluoroplastics, polythiol resins, and cationically polymerizable epoxy resins. Still further, the base materials may be photo- and chemical-polymerizable monomers and oligomers, and more specifically ethylenically unsaturated compounds. Concrete examples include acrylic or methacrylic esters of mono- or polyhydric alcohols, and 4-methacryloyloxy group-containing aromatic polycarboxylic acids and anhydrides thereof. These can be used alone or as a combination of two or more thereof. Where the monomer is used as the base material, no influence is left even if the near infrared ray-decolorizable recording material is dissolved in the monomer and the mixture then chemically polymerized or photopolymerized. The base material according to the present invention is not limited thereto, and all materials are applicable as long as they can be mixed with the near infrared ray-decolorizable recording material by dissolving or dispersing.

The near infrared ray-decolorizable recording material of the present invention can be formed by dissolving with a solvent or by melting, and mixing with the base material in a ratio of 0.01 to 90% by weight, particularly 0.1 to 50% by weight. Note, the near infrared ray-decolorizable recording material of the present invention can give a desired effect even when the near infrared ray-decolorizable recording material itself is dissolved in a solvent and then coated or set.

The decolorization of the near infrared ray-decolorizable recording material of the present invention can be further promoted by adding a quaternary ammonium-borate complex having the formula (II) as a sensitizer:



wherein R_5 , R_6 , R_7 , and R_8 independently represent an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, heterocyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_5 , R_6 , R_7 , and R_8 represents an alkyl group having 1 to 8 carbon atoms; and

R_9 , R_{10} , R_{11} , and R_{12} independently represent hydrogen, an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, or substituted alkynyl. Examples of the substituent groups are methyl, ethyl, n-propyl, n-butyl, n-hexyl, cyclohexyl, cyclohexenyl, methoxymethyl, methoxyethyl, dimethylaminoethyl, phenyl, anisyl, ethoxyphenyl, methylphenyl, tert-butylphenyl, fluorophenyl, chlorophenyl, dimethylaminophenyl, diethylaminophenyl, vinyl, allyl, isobutylsilyl, dimethylphenylsilyl, diethylphenylsilyl, trimethylsilyl, hydrogen, heterocyclic, phenyl, silyl, cytidyl, etc.

Typical examples include tetramethylammonium n-butylphenyl borate, tetramethylammonium n-

To improve the compatibility of the linear binder with the near infrared ray-decolorizable recording material or the quaternary ammonium-borate complex sensitizer, and the decolorization speed, it is

EP 0 468 465 A1

Fillers similar to those of the above-mentioned decolorizable toner for electrophotography may be used, and conventional ultraviolet absorbing agents may be used as the ultraviolet absorbing agent.

To improve the decolorizing speed, a plasticizer which can be used for modifying a resin, as in the case of the decolorizable toner, or a sensitizer and wax which are used in a thermal recording paper can be used.

The near infrared ray-decolorizable recording material, which is a colorant for the decolorizable printing ink, may be mixed with the above-mentioned vehicle in a ratio of 0.01 to 90% by weight, preferably at a ratio of 0.5 to 20% by weight. The addition of the quaternary ammonium-octate complex sensitizer in an amount of 0.01 to 10% by weight, preferably 0.1 to 5% by weight, based on one percent by weight of the near infrared ray-decolorizable recording material, enhances the decolorization speed. The resin may be mixed so as to meet the requirement of the printing operation.

The fillers also may be added in an amount of 1 to 20% by weight, preferably 1 to 5% by weight. The ultraviolet absorbing agent may be added in an amount of 1 to 20% by weight based on the weight of the drying oil.

This decolorizable printing ink can be prepared by kneading the near infrared ray-decolorizable recording material of the present invention with the drying oil, and if required, adding and kneading the quaternary ammonium-borate complex sensitizer, ultraviolet absorbing agent, fillers, etc.

After being printed by any of various printing processes, such as off-set press printing, letterpress printing, gravure press printing, transfer press printing, or a specific press printing inclusive of flexographic printing, metal printing, plastic printing, and glass printing, as well as electric printing by printers such as an impact printers or non-impact printers, this decolorizable printing ink can be decolorized by irradiating near infrared rays by a semiconductor laser, a halogen lamp, or a luminescent semiconductor diode. Further, the decolorized portion can be repeatedly printed.

As an example of the application of a thermal melt-transfer sheet, a transfer film comprising the near infrared ray-decolorizable recording material kneaded with a paraffin wax as a binder and a xylene resin as a flexibilizer coated on a PET film is brought into close contact with a recording paper, and transferred and printed by a heated head. This set portion can be decolorized by irradiating near infrared rays.

According to the present invention, a near infrared ray-decolorizable recording material, decolorizable toner and a decolorizable ink, which can be decolorized with near infrared rays after being set and printed, which can be repeatedly printing on the same portion, and which is stable under visible light, is provided.

The present invention will now be described with reference to the following Examples, which in no way limit the scope of the present invention.

Example 1

A 20 parts by weight amount of polymethyl methacrylate were dissolved in 73 parts by weight of methyl ethyl ketone, and the near infrared ray-decolorizable recording material listed in Table 2 was dissolved and mixed therein, in the amount shown in Table 2, to obtain a composition.

Example 2

A 20 parts by weight amount of polymethyl methacrylate were dissolved in 75 parts by weight of methyl ethyl ketone, and the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2 were dissolved and mixed therein, in the amount shown in Table 2, to obtain a composition.

Example 3

A 20 parts by weight amount of polystyrene were dissolved in 75 parts by weight of toluene, and the near infrared ray-decolorizable recording material shown in Table 2 was dissolved and mixed therein, in the amount shown in Table 2, to obtain a composition.

Example 4

A 20 parts by weight amount of polystyrene were dissolved in 70 parts by weight of toluene, and the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2 were dissolved and mixed therein, in the amounts shown in Table 2, to obtain a composition.

Example 5

A 20 parts by weight amount of polymethyl methacrylate were dissolved in 76 parts by weight of methyl ethyl ketone, and near infrared ray-decolorizable recording material shown in Table 2 in the amount shown in Table 2 and 2 parts by weight of SO red 1 (supplied by Orient Kagaku Kogyo) were dissolved and mixed therein, to obtain a composition.

Example 6

A 20 parts by weight amount of polymethyl methacrylate were dissolved in 74 parts by weight of methyl ethyl ketone, and near infrared ray-decolorizable recording material shown in Table 2 in the amount shown in Table 2 and 2 parts by weight of Oil Yellow (supplied by Orient Kagaku Kogyo) were dissolved and mixed therein, to obtain a composition.

Example 7

In 20 parts by weight of paraffin wax (melting point: 69°C) was thermally melted the near infrared ray-decolorizable recording material shown in Table 2 in the amount shown in Table 2, at 80°C to obtain a composition.

Example 8

In 70 parts by weight of paraffin wax (melting point: 69°C) were thermally melted the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2 in the amount shown in Table 2, at 80°C to obtain a composition.

Example 9

In 60 parts by weight of trimethylolpropane triacrylate was dissolved and mixed the near infrared ray-decolorizable recording material shown in Table 2 in the amount shown in Table 2, and 10 parts by weight of methyl o-benzylbenzoate and 5 parts by weight of triethanol amine were added, to obtain a composition.

Example 10

In 45 parts by weight of trimethylolpropane triacrylate were dissolved and mixed the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2 in the amount shown in Table 2, and further 10 parts by weight of methyl o-benzylbenzoate and 5 parts by weight of triethanol amine were added, to obtain a composition.

Examples 11 and 12

In 98 parts by weight of hydrogenated polystyrene (softening point: 101°C) was dissolved and kneaded near infrared ray-decolorizable recording material shown in Table 2 in the amount shown in Table 2 using methylene chloride, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Examples 13 to 17

In 98 parts by weight of styrene-butyl methacrylate copolymer (softening point: 72°C) were dissolved and kneaded the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2 in the amount shown in Table 2 using methylene chloride, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Examples 18 to 20

In 94 parts by weight of styrene-butyl methacrylate copolymer (softening point: 72°C) were dissolved and kneaded the near infrared ray-decolorizable recording material, the sensitizer and the electrostatic charge regulator shown in Table 2 in the amount shown in Table 2 using methylene chloride, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill,

and then finely pulverized with a jet mill to prepare a toner.

Examples 21 to 23

15 In 89 parts by weight of styrene-butyl methacrylate copolymer (softening point 72° C) were dissolved and kneaded the near infrared ray-decolorizable recording material, the sensitizer, the electric charge regulator and the plasticizer shown in Table 2 in the amount shown in Table 2 using methylene chloride, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Examples 24 and 25

15 In 94 parts by weight of styrene-butyl methacrylate copolymer (softening point 72° C) were dissolved and kneaded the near infrared ray-decolorizable recording material, the sensitizer and the electric charge regulator shown in Table 2 in the amount shown in Table 2 using methylene chloride, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Examples 26 and 27

20 In 91 parts by weight of polymethyl methacrylate (softening point: 78° C) were dissolved and kneaded the near infrared ray-decolorizable recording material, the sensitizer, and the electric charge regulator shown in Table 2 in the amount shown in Table 2 and a methylene chloride dispersion containing 3 parts by weight of titanium white as an additive, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Example 28

20 In 89 parts by weight of polymethyl methacrylate (softening point: 78° C) were dissolved and kneaded the near infrared ray-decolorizable recording material, the sensitizer and the electric charge regulator shown in Table 2 in the amount shown in Table 2 and a methylene chloride dispersion containing 2 parts by weight of a ultraviolet absorbing agent (supplied by Sumitomo Chemical Industries, SUMISORB 400) and 3 parts by weight of titanium white as additives, after which methylene chloride was removed. The resulting mixed resin was coarsely pulverized with a hammer mill or a cutter mill, and then finely pulverized with a jet mill to prepare a toner.

Examples 29 and 30

25 In 60 parts by weight of linseed oil and 30 parts by weight of styrene-maleic acid resin (softening point: 70° C) was dissolved and kneaded the near infrared ray-decolorizable recording material shown in Table 2, in the amount shown in Table 2, to prepare an ink.

Examples 31 to 35

25 In 50 parts by weight of linseed oil and 30 parts by weight of styrene maleic acid resin (softening point: 70° C) were dissolved and kneaded the near infrared ray-decolorizable recording material and the sensitizer shown in Table 2, in the amount shown in Table 2, to prepare an ink.

Examples 36 to 38

30 In 40 parts by weight of soybean oil and 30 parts by weight of acrylic resin (softening point: 65° C) was kneaded the near infrared ray-decolorizable recording material, the sensitizer, and the solvent shown in Table 2, in the amount shown in Table 2, to prepare an ink.

Examples 39 to 41

35 In 40 parts by weight of soybean oil and 25 parts by weight of acrylic resin (softening point: 65° C) were

included the near infrared ray-decolorizable recording material, the sensitizer, the solvent and the plasticizer shown in Table 2, in the amount shown in Table 2, to prepare an ink.

Method to Evaluating Decolorizing Properties

Concerning the compositions of Examples 1 to 8, 0.5 g of these compositions were drawn down on a Carton paper by using an RI tester, to obtain samples. The compositions of Examples 7 and 8 were coated on a polyethyleneterephthalate film having a thickness of 3.5 microns by a wire bar, to attain a membrane thickness of 4 microns. The sheets were transferred and set on a recording paper by a thermal printer at an applied energy of 2.0 mJ/dot, to obtain samples. Concerning the compositions of Examples 9 and 10, 0.5 g thereof were drawn down on a Carton paper by using an RI tester, and cured by irradiation of a ultraviolet ray for 1 minute, by an 80 W/cm metal halide lamp at a distance of 8 cm.

The toners obtained in Examples 11 to 28 were further subjected to a surface treatment with a hydrophobic silica and then a carrier was mixed thereto, after which they were set on a PPC paper by a copy machine for PPC (Model LCS-24 supplied from Casio), to obtain samples.

The inks obtained in Examples 29 to 41 were drawn down on a Carton paper in amount of 5 g by using an RI tester, to obtain samples.

By irradiating near infrared rays generated from an aluminum coat type halogen lamp (2W/cm²) on the samples, for one minute, the decolorization was evaluated. The results of the evaluation are shown in Table 3.

Method of Evaluation of Resistance to Visible Light

Samples were made in the same manner as for the method of evaluating the decolorizing properties. The samples were irradiated by a dichroic coat type halogen lamp (2W/cm²) using an infrared cut filter, for 1 hour, to evaluate the decolorization.

EP 0 468 465 A1

Table 2

Near Infrared-Ray Decolorizable Recording Material (Complex No. in Table 1) and Other Additives		Amount (% by weight)
Example 1	Complex 3A	2
Example 2	Complex 3A	2
	Sensitizer (TBAPB)	2
Example 3	Complex 5B	5
Example 4	Complex 5B	5
	Sensitizer (TMAPB)	5
Example 5	Complex 7C	2
Example 6	Complex 7C	2
	Sensitizer (TBAB3)	2
Example 7	Complex 3A	20
Example 8	Complex 3A	20
	Sensitizer (TBAPB)	10
Example 9	Complex 9	30
Example 10	Complex 9	30
	Sensitizer (TBAPB)	15
Example 11	Complex 2	2
Example 12	Complex 3C	2
Example 13	Complex 3A	0.5
	Sensitizer (TBAPB)	2
Example 14	Complex 3A	2
	Sensitizer (TBAPB)	2

EP 0 468 485 A1

Table 2 (Continued)

	Near Infrared-Ray Decolorizable Recording Material (Complex No. in Table 1) and Other Additives	Amount (g by weight)
Example 15	Complex 3A	5
	Sensitizer (TBAPS)	2
Example 16	Complex 3C	2
	Sensitizer (TMAPS)	2
Example 17	Complex 6B	2
	Sensitizer (TBAPS)	2
Example 18	Complex 3A	2
	Sensitizer (TBAPS)	2
	Electric charge regulator (Kayacharge N1 supplied from Nippon Kayaku)	2
Example 19	Complex 6A	2
	Sensitizer (TBAPS)	2
	Electric charge regulator (Kayacharge N1 supplied from Nippon Kayaku)	2
Example 20	Complex 7A	2
	Sensitizer (TMAPS)	2
	Electric charge regulator (Bontren E 89 supplied from Orient Kagaku Kogyo)	2
Example 21	Complex 3A	2
	Sensitizer (TBAPS)	2
	Electric charge regulator (Bontren E 89 supplied from Orient Kagaku Kogyo)	2
	Plasticizer (Dibutyl phthalate)	5

EP 0 468 485 A1

Table 2 (Continued)

	Near Infrared-Ray Decolorizable Recording Material (Complex No. in Table 1) and Other Additives	Amount (% by weight)
Example 22	Complex 7A	2
	Sensitizer (TBAPB)	2
	Electric charge regulator (Bontron E 89 supplied from Orient Kagaku Kogyo)	2
	Plasticizer (Ethyl stearate)	5
Example 23	Complex 1C	2
	Sensitizer (TBABB)	2
	Electric charge regulator (Bontron E 89 supplied from Orient Kagaku Kogyo)	2
	Plasticizer (Diethyl terephthalate)	5
Example 24	Complex 3A	2
	TBAPB	2
	Electric charge regulator (Kayacharge N1 supplied from Nippon Kayaku)	2
Example 25	Complex 9	2
	TBABB	2
	Electric charge regulator (Bontron E 89 supplied from Orient Kagaku Kogyo)	2
Example 26	Complex 3A	2
	TBAPB	2
	Electric charge regulator (Kayacharge N1 supplied from Nippon Kayaku)	2

Table 2 (Continued)

5	Near Infrared-Ray Decolorizable Recording Material (Complex No. in Table 1) and Other Additives	Amount (% by weight)
10	Example 27	Complex 6C 2 TMHPS 2 Electric charge regulator 2 (Bontron Z 89 supplied from Orient Kagaku Kogyo)
15	Example 28	Complex 3B 2 TBAPS 2 Electric charge regulator 2 (Kayacharge N1 supplied from Nippon Kayaku)
20	Example 29	Complex 3A 10
25	Example 30	Complex 6C 10
30	Example 31	Complex 3A 2 Sensitizer (TBAPS) 10
35	Example 32	Complex 3A 10 Sensitizer (TBAPS) 10
40	Example 33	Complex 3A 20 Sensitizer (TBAPS) 10
45	Example 34	Complex 7C 10 Sensitizer (TMAPS) 10
50	Example 35	Complex 9 10 Sensitizer (TBAPS) 10

50

55

EP 0 468 465 A1

Table 2 (Continued)

	Near Infrared-Ray Decolorizable Recording Material (Complex No. in Table 1) and Other Additives	Amount (% by weight)
Example 36	Complex 3A	10
	Sensitizer (TBAPS)	10
	Solvent (Toluene)	10
Example 37	Complex 5A	10
	Sensitizer (TBABB)	10
	Solvent (Ethylene Glycol Monoethyl ether)	10
Example 38	Complex 7A	10
	Sensitizer (TMHPB)	10
	Solvent (Polyethylene Glycol)	10
Example 39	Complex 3A	10
	Sensitizer (TBAPS)	10
	Solvent (Toluene)	10
	Plasticizer (Dibutyl phthalate)	5
Example 40	Complex 7A	10
	Sensitizer (TBAPS)	10
	Solvent (Ethylene Glycol Monoethyl ether)	10
	Plasticizer (Ethyl stearate)	5
Example 41	Complex 3A	10
	Sensitizer (TBABB)	10
	Solvent (Polyethylene Glycol)	10
	Plasticizer (Diethyl terephthalate)	5

Note: TMAPS: Tetramethylammonium n-butyltriphenyl borate
 TBAPS: Tetrabutylammonium n-butyltriphenyl borate
 TMHPB: Triethylhydrogenammonium n-butyltriphenyl borate
 TBABB: Tetrabutylammonium tetra-n-butyl borate

EP 0 462 465 A1

Table 1

5

Hue of Sample

10

15

20

25

30

35

40

45

50

55

Example	Before Irradiation	After Irradiation with Near infrared rays	After Irradiation with Visible rays
1	Blue	Transparent	Not Changed
2	Blue	Transparent	Not Changed
3	Blue	Transparent	Not Changed
4	Blue	Transparent	Not Changed
5	Purple	Red	Not Changed
6	Green	Yellow	Not Changed
7	Blue	White	Not Changed
8	Blue	White	Not Changed
10	Blue	Transparent	Not Changed
11	Blue	Transparent	Not Changed
12	Blue	Transparent	Not Changed
13	Blue	Transparent	Not Changed
14	Blue	Transparent	Not Changed
15	Blue	Transparent	Not Changed
16	Blue	Transparent	Not Changed
17	Blue	Transparent	Not Changed
18	Blue	Transparent	Not Changed
19	Blue	Transparent	Not Changed
20	Blue	Transparent	Not Changed
21	Blue	Transparent	Not Changed

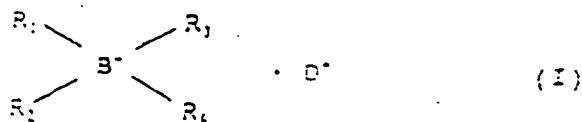
EP 0 468 465 A1

Table 3 (Continued)

Example	Hue of Sample		
	Before Irradiation	After Irradiation with Near Infrared rays	After Irradiation with Visible rays
22	Blue	Transparent	Not Changed
23	Blue	Transparent	Not Changed
24	Blue	Transparent	Not Changed
25	Blue	Transparent	Not Changed
26	Blue	White	Not Changed
27	Blue	White	Not Changed
28	Blue	White	Not Changed
29	Blue	Transparent	Not Changed
30	Blue	Transparent	Not Changed
31	Blue	Transparent	Not Changed
32	Blue	Transparent	Not Changed
33	Blue	Transparent	Not Changed
34	Blue	Transparent	Not Changed
35	Blue	Transparent	Not Changed
36	Blue	Transparent	Not Changed
37	Blue	Transparent	Not Changed
38	Blue	Transparent	Not Changed
39	Blue	Transparent	Not Changed
40	Blue	Transparent	Not Changed
41	Blue	Transparent	Not Changed

Claims

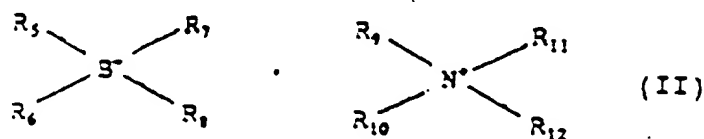
1. A near infrared ray-decolorable recording material comprising a near infrared ray-absorbing cationic dye-borate anion complex having the formula (I):



wherein D^+ represents a cationic dyestuff having absorptions in the near infrared region;

R_1 , R_2 , R_3 , and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_1 , R_2 , R_3 , and R_4 represent an alkyl group having 1 to 8 carbon atoms.

2. A near infrared ray-decolorizable recording material as claimed in claim 1 further comprising a sensitizer having the formula (II):

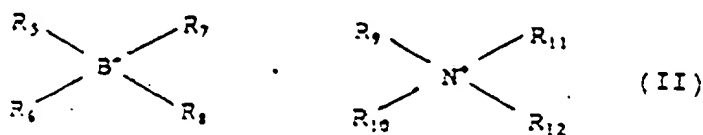


wherein R_5 , R_6 , R_7 , and R_8 independently represent an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_5 , R_6 , R_7 , and R_8 represent an alkyl group having 1 to 8 carbon atoms; and

R_9 , R_{10} , R_{11} , and R_{12} independently represent hydrogen, an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, or substituted alkynyl.

3. A decolorizable toner comprising a near infrared ray-decolorizable recording material according to claim 1 as a colorant, in which a set portion is decolorized with near infrared rays.

4. A decolorizable toner as claimed in claim 3, further comprising a sensitizer having the formula (II):

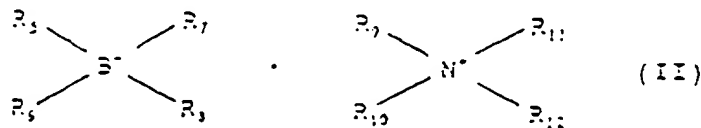


wherein R_5 , R_6 , R_7 , and R_8 independently represent an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_5 , R_6 , R_7 , and R_8 represent an alkyl group having 1 to 8 carbon atoms; and

R_9 , R_{10} , R_{11} , and R_{12} independently represent hydrogen, an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, or substituted alkynyl.

5. A decolorizable ink comprising a near infrared ray-decolorizable recording material according to claim 1 as a colorant, in which a set portion is decolorized with near infrared rays.

6. A decolorizable ink as claimed in claim 5, further comprising a sensitizer having the formula (II):



EP 0 468 465 A1

wherein R_5 , R_6 , R_7 , and R_8 independently represent an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, alicyclic, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, substituted alkynyl, or substituted silyl, with the proviso that at least one of R_5 , R_6 , R_7 , and R_8 represent an alkyl group having 1 to 8 carbon atoms; and

R_9 , R_{10} , R_{11} , and R_{12} independently represent hydrogen, an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, or saturated or unsaturated heterocyclic group, substituted alkyl, substituted aryl, substituted alkaryl, substituted allyl, substituted aralkyl, substituted alkenyl, or substituted alkynyl.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 2356

DOCUMENTS CONSIDERED TO BE RELEVANT

DOCUMENTS REFERENCED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
P, X	EP-A-0 379 167 (FUJI PHOTO) • abstract • • page 2, line 43 - line 55 • • page 9, line 25 - line 35 • • Database WPI, no. 90-225779, Derwent Publications Ltd., London, GB, & JP-A-2187762 (FUJI) 23-07-1990 • Abstract •	1,2	C03G3/00 C09013/00
X	— EP-A-0 040 977 (3M) • page 3, line 10 - line 35 • • page 4, line 27 - page 6, line 15; claims 1-16 •	1,2	
A	— EP-A-0 305 054 (CANON KABUSHIKI KAISHA) • page 5, line 15 - line 47 •	1-7	
A	— PATENT ABSTRACTS OF JAPAN vol. 14, no. 197 (P-J038)(4134) 18 April 1990 & JP-A-02 037 364 (MITA IND CO LTD) 7 February 1990 • abstract •	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	— EP-A-0 223 587 (THE MEAD CORPORATION) • page 8; example 4 •	1-7	C03G C11B C090
The present search report has been drawn up for all claims			
Name of applicant THE HAGUE		Date of completion of the search 31 OCTOBER 1991	
Name of inventor THE HAGUE		Name of agent VOGT, CANOLA	
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if cited alone Y: particularly relevant if combined with another document of the same category A: background art O: non-written disclosure P: prior art		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date O: document cited in the application L: document cited for other reasons A: document of the same patent family, corresponding document	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.